

DEHYDROGENATION OF ITSL COAL, COAL EXTRACT, AND PROCESS SOLVENT

R. P. Skowronski, L. A. Heredy, L. R. McCoy, J. J. Ratto,* and M. B. Neuworth**

Rockwell International, Rocketdyne Division, 6633 Canoga Avenue,
Canoga Park, CA 91304

*Rockwell International, Science Center, 1049 Camino Dos Rios,
Thousand Oaks, CA 91360

**Mitre Corporation, 1820 Dolley Madison Blvd., McLean, Virginia 22102.

INTRODUCTION

Catalytic dehydrogenation is an important method for determining the hydroaromatic contents of coals, coal extracts, and process solvents. Past investigations by others have focused on the dehydrogenation of coal.(1-4) Most of that work was conducted with phenanthridine because it is a relatively good solvent for coal and, at its boiling point, catalytic dehydrogenation usually proceeds at a rapid rate. However, a literature survey carried out by Neuworth has shown that secondary reactions such as those involving oxygenated structures had a significant impact on dehydrogenation results at elevated temperatures.(5) Consequently, in the present work, we have attempted to identify other, lower-boiling solvents suitable for dehydrogenation in order to minimize secondary reactions.

The objective of the work described in this preprint was to develop a refined dehydrogenation method and apply it to investigate the hydroaromatic contents of the coal, coal extract, and process solvent used in the Integrated Two-Stage Liquefaction (ITSL) process. Determination of the hydroaromatic contents of these materials is important in order to achieve an understanding of the structure of these materials and obtain an insight into the chemistry of the process. Furthermore, catalytic dehydrogenation is one of the best ways to determine the donor quality of a process solvent.

EXPERIMENTAL

The desired amount of substrate, depending on its estimated hydrogen content (e.g., about 0.25 g for tetralin), is weighed into a 40-ml flask. Next, 7.50 g of the selected solvent, 0.55 g of catalyst (5 wt. % Pd on CaCO_3), and a pyrex-encased Alnico stirrer are introduced into the flask. The dehydrogenation system is then assembled as described in detail in Reference 6. This system was designed to provide for automatic data recording. Such capability is particularly useful in experiments which require overnight operation. Connections from the gas collection burette are made of glass to minimize diffusion losses of hydrogen. Gas sampling is provided for by a gas collection port.

Key to the unattended operation of this equipment is the mercury pressure switch. As gas is evolved by dehydrogenation of the sample, the small increase in pressure actuates the switch. When this occurs, the circuitry in the motor/switch interface box turns on the motor for a 10-s interval. The motor is connected to a threaded rod carrying the leveling tube. Rotation of the rod repositions the bulb to balance the pressure increase. The top of the rod is attached to a 10-turn potentiometer through a reducer (48:1) which reduces the number of turns required to achieve leveling to the 10-turn capability of the potentiometer. Fifteen volts are imposed across the potentiometer by a precision power supply located in the motor/switch interface box. By connecting the potentiometer wiper and the neutral lead to the recorder, the output voltage can be employed to define the position of the leveling bulb. Consequently, it provides a continuous recording of the gas volume within the gas collection tube.

Elemental analysis to determine C, H, N, S, and O content was performed using a Perkin-Elmer Model 240C elemental analyzer. Number-average molecular weights of the distillate fractions were determined using vapor-phase osmometry (VPO). The molecular weight determinations as well as the elemental analyses were conducted by Galbraith Laboratories, Inc.

Proton nuclear magnetic resonance (^1H NMR) spectra were obtained with a JEOL FX-60-Q Fourier transform NMR spectrometer using an observation frequency of 59.79 MHz. The spectra were recorded with an internal deuterium lock system. The NMR samples and reference were contained in 10-mm tubes, with a probe temperature of 30°C. Chloroform- d was the solvent used. A 45° pulse, which corresponds to 14 μs , was used during multiple-scan accumulation. The pulse repetition time was 6.0 s. The ^1H spectra are referenced to tetramethylsilane (TMS) at 0.0 ppm chemical shift (δ).

The ^{13}C NMR spectra were recorded using ^1H -decoupling with an internal deuterium lock system utilizing 10-mm sample tubes. A 45° pulse was used during multiple scan accumulation corresponding to 6 μs . The pulse repetition time was 2.0 s. The samples were dissolved in chloroform- d ; the spectra were referenced to the center peak of the solvent at 77.0 ppm and tetramethylsilane at 0.0 ppm.

RESULTS AND DISCUSSION

The initial experiments were conducted with model compounds. Tetralin (1,2,3,4-tetrahydronaphthalene), 1,2,3,4,5,6,7,8-octahydrophenanthrene, and 9,10-dihydroanthracene were used as substrates. Durene, 2-methylnaphthalene, and quinoline were tested as solvents. Quinoline was found to give the fastest rate of dehydrogenation and was used in most subsequent experiments.⁽⁶⁾

The middle distillation fraction (750-850°F) of the ITSL process solvent (Illinois No. 6 coal, 8-in. PDU BTMS Run 108, 80/20 blend, June 17, 1983) was selected as the next material for investigation by dehydrogenation. It was chosen because prior characterization by proton NMR had shown that it contained a substantial percentage of hydroaromatic compounds. Approximately 3 g of this material was dehydrogenated using 1.1 g of Pd catalyst in 15 g of quinoline. The gas evolution rate was approximately 0.15 ml/min during the first day, and the experiment was allowed to continue until the rate decreased to about 20% of that observed initially. After 5 days, the experiment was terminated on this basis. A total of 270 ml of gas was obtained. Based on the elemental analysis of this solvent fraction and the quantity used, it was calculated that 11% of the total hydrogen in the sample was collected.

Elemental analysis of the dehydrogenated process solvent showed an 11% loss of hydrogen, which is consistent with the 11% loss that was calculated based on the volume of gas collected and the sample amount. The number-average molecular weight determined by VPO for the original and dehydrogenated process solvent were 263 and 259, respectively. This result indicates that, as expected, the dehydrogenation procedure had no significant effect on the number-average molecular weight.

The proton NMR spectra of the original distillation fraction of the process solvent and of the dehydrogenated material are shown in Figures 1 and 2, respectively. An increase in the aromatic portion of the sample and a decrease in the aliphatic portion as a result of the dehydrogenation procedure are evident. This qualitative result is confirmed by Table 1 which presents the results of the integration of the spectra over characteristic proton regions.

Changes in the carbon distribution of the process solvent fraction as a result of dehydrogenation were determined by analyses of the carbon-13 NMR spectra. The data are shown in Table 2. These data give additional support to the observation of an increase in aromatic protons at the expense of the aliphatic protons by indicating an increase in the aromatic carbon at the expense of the aliphatic carbon.

A more detailed evaluation of the spectra was made to obtain additional information with regard to the main reactions that take place during catalytic dehydrogenation. It was determined that, although the intensity of the well-defined β -aliphatic absorption at 1.86 ppm was strongly reduced (indicating the dehydrogenation of tetralin-like structures), mostly α -aliphatic protons were eliminated during dehydrogenation. The most probable structures of this type which can participate in the dehydrogenation reaction are 9,10-dihydrophenanthrene and 4,5-dihdropyrene. The chemical shift of the $-\text{CH}_2-\text{CH}_2-$ group of 9,10-dihydrophenanthrene is 2.86 ppm. The chemical shift of this group in 4,5-dihdropyrene is not available.

The data indicate that a typical reaction which takes place in this system on catalytic dehydrogenation is the loss of hydrogen from 4,5-dihdropyrene-type structures with the ultimate formation of pyrene or chrysene derivatives or some other similar, more highly condensed aromatic compounds. To distinguish between smaller (1-3 rings) and larger (4+ rings) condensed aromatic systems, the aromatic absorption area was divided into two sections at the chemical shift value of 7.85 ppm, which corresponds to a minimum between two absorption peaks at about 7.7 ppm and 8.0 ppm. This division applies to most condensed aromatic hydrocarbons. (Anthracene is one exception; it has about equal absorptions in both regions.) The relative absorption intensities in these sections of the spectra of the untreated and the dehydrogenated process solvent fractions are shown in Table 3. As a result of the dehydrogenation, a considerable shift toward larger condensed aromatic structures has taken place.

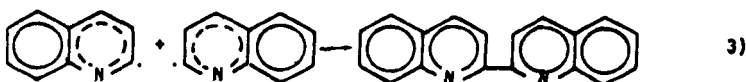
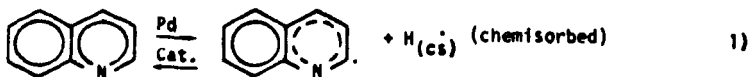
It was hypothesized that if a coal is first partially dehydrogenated and then subjected to depolymerization, this reaction sequence may make it possible to distinguish between cyclic and acyclic CH_2 -bridges in the coal. Cyclic bridge structures would be rendered inert to depolymerization because of aromatization in the dehydrogenation reaction. Therefore, the benzene-soluble fraction from the depolymerization of a dehydrogenated coal would contain fewer CH_2 -bridges than the same product of the direct depolymerization of coal. A coal dehydrogenation/-depolymerization experiment was therefore conducted, and the products were separated by solvent fractionation.⁽⁶⁾

Depolymerization of the dehydrogenated coal yielded 10% more benzene-soluble product containing 36% more CH_2 -bridges than the depolymerization of the untreated coal. Since catalytic dehydrogenation would have converted at least a fraction of the cyclic CH_2 -bridges to nonreactive aromatic structures, the increased amount of CH_2 -bridges identified in the benzene-soluble fraction indicate that they originate from acyclic bridge structures in the coal. It is possible that a few more reactive acyclic CH_2 -bridges have formed by the catalytic dehydrogenation of hydroaromatic rings linked to acyclic CH_2 -bridges in the coal. Assuming that each acyclic CH_2 -bridge is linked to aromatic/hydroaromatic ring structures corresponding to a total formula weight of 450, these acyclic CH_2 -bridges form the linkage in about 10 wt. % of the organic coal material.

Several control experiments were conducted with quinoline and catalyst (i.e., without a substrate) in parallel with the experiments described above.⁽⁶⁾ The main conclusions from these experiments are: (1) under these conditions evolution of H_2 occurs; (2) such H_2 evolution is believed to be due to the dimerization

of quinoline on the basis of GC-MS data; (3) the rate of dimerization of quinoline depends on the H_2 concentration of the atmosphere above the reactant; (4) consequently, the dimerization rate is greatly reduced when the inert gas atmosphere is replaced with H_2 ; (5) the dimer formation is not reversible under the conditions of the dehydrogenation reaction, the dimer will slowly accumulate in the system; (6) quinoline can be catalytically hydrogenated to form THQ in this reactor system at a temperature below the boiling point of quinoline; and (7) the presence of the process solvent suppresses hydrogen release by the quinoline. Conclusion (7) is supported by the fact that the quantity of gas evolved during the dehydrogenation of the process solvent fraction agreed well with the differences in the hydrogen contents of the original and dehydrogenated materials. The presence of hydrogen from the substrate in the system markedly reduces the hydrogen contribution from the quinoline dimerization.

A tentative reaction schematic of the quinoline dimerization reaction can be written as follows:



Reactions 1) and 2) are reversible. Therefore, increased H_2 partial pressure reduces the rate of formation of the quinolinyl radical, and thus, also the rate of formation of the dimer. Reaction 3) is not reversible. Therefore, the dimer will slowly accumulate in the solution, with the rate of dimer formation depending on the hydrogen pressure.

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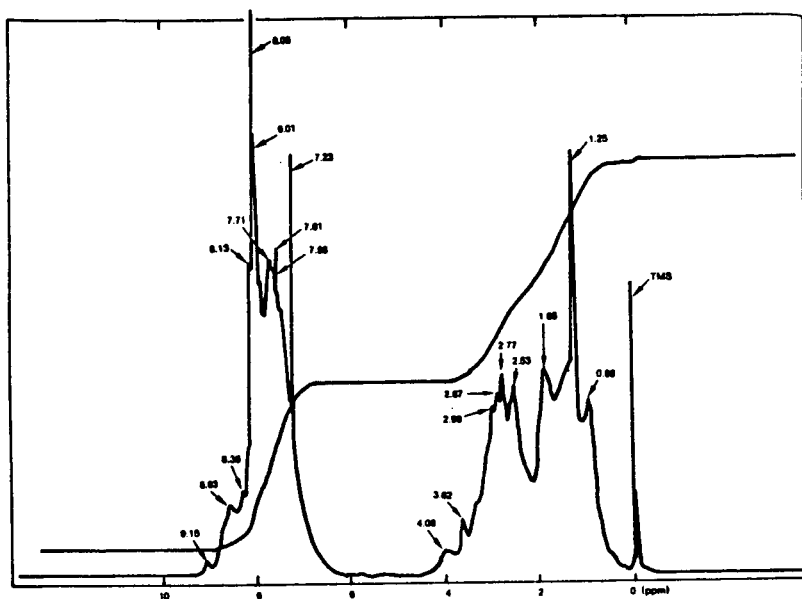


Figure 1. Proton NMR Spectrum of 750 to 850°F Fraction of Process Solvent

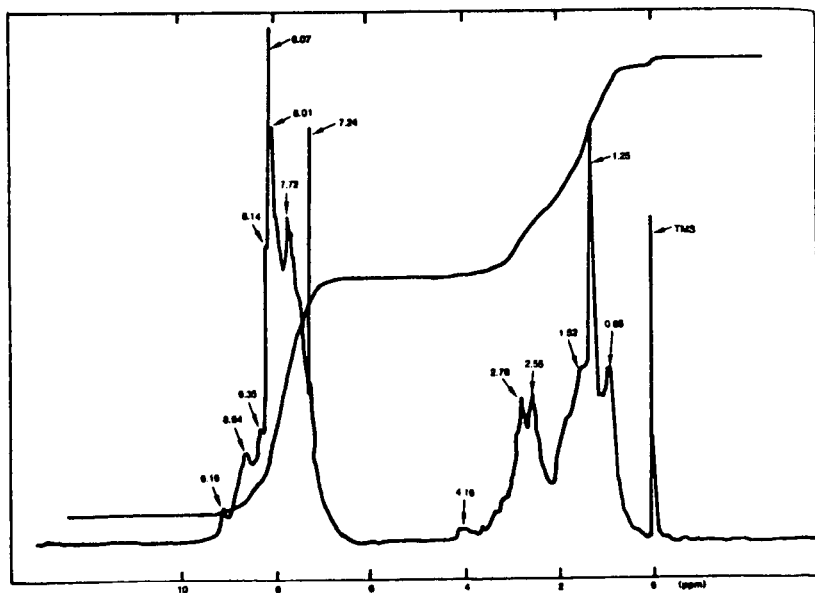


Figure 2. Proton NMR Spectrum of Dehydrogenated 750 to 850°F Fraction of Process Solvent

TABLE 1
PROTON-TYPE DISTRIBUTIONS OF ORIGINAL AND
DEHYDROGENATED PROCESS SOLVENT FRACTION*

Structural Region	Original Solvent (%)	Dehydrogenated Solvent (%)
Aromatic 6.0 to 10.0 ppm	44	52
α -Aliphatic 2.0 to 4.5 ppm	25	17
β -Aliphatic 1.0 to 2.0 ppm	29	28
γ -Aliphatic 0.0 to 1.0 ppm	2	3

*750 to 850°F

TABLE 2
CARBON DISTRIBUTION IN THE PROCESS
SOLVENT FRACTION* BEFORE AND AFTER
DEHYDROGENATION

Carbon Distribution	Original Fraction (%)	Dehydro- genated (%)
C _{Al} (0-68 ppm)	28	18
C _{Ar} (108-200 ppm)	72	82
C _{HA} (22-31 ppm)	15	9

*750-850°F

TABLE 3
AROMATIC PROTON-TYPE DISTRIBUTION OF
ORIGINAL AND DEHYDROGENATED PROCESS
SOLVENT FRACTION

Structural Region	Original Solvent (%)	Dehydro- genated Solvent (%)
Aromatic (1-3 rings, 6.9-7.85 ppm)	55	43
Aromatic (4+ rings, 7.85-9.2 ppm)	45	57